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J. M. Honig

Elements of the Hijmans-deBoer Approximation to Order-Disorder Theory

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ABSTRACT

In this report the Hijmans-de Boer approximation scheme to order-disorder theory is reviewed, with special reference to its ultimate application in the area of gas adsorption phenomena. The purpose of the exposition is to provide a more detailed description of the derivation and to assist the reader, wherever possible, in visualizing the fundamental scheme by a pictorial approach.

Accepted for the Air Force
Stanley J. Wisniewski
Lt Colonel, USAF
Chief, Lincoln Laboratory Office

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ELEMENT OF THE HIJMANS-DE BOER APPROXIMATION TO ORDER-DISORDER THEORY

I. INTRODUCTION

In recent years the theory pertaining to gas adsorption in localized monolayers in the presence of lateral interactions has been put on a systematic basis, using order-disorder theory.[1-3] For this purpose the Hijmans-de Boer formulation[4] of order-disorder phenomena has been extremely useful. While mathematically not as elegant as some other methods described in the literature (for a general survey see Refs. 5 and 6), it possesses the definite advantage of being relatively simple and amenable to pictorial representation. Unfortunately, in the original publications[4] as well as in the later applications[1-3] sufficient space was not available for a full exposition of the Hijmans-de Boer methodology. Therefore, it does not seem inappropriate to deal in greater detail with the fundamental structure of the Hijmans-de Boer theory; particularly since the basic concepts can be applied to other areas (e.g., ferromagnetism, binary alloys) without change. For the application of the theory to adsorption phenomena, the reader is directed to the original articles and to a recent review.[7]

For gas adsorption processes analyzed with this method, one deals with models in which the surface of a solid is represented by a regular array of adsorption sites, each of which is either full (occupied) or empty (unoccupied). Assuming that the various sites are energetically equivalent, and that each adsorbate molecule is held to a given site, one wishes to determine the surface coverage and the thermodynamic properties of the adlayer as a function of the pressure of the gas in equilibrium with it. In the solution of this problem one must allow for the possibility of lateral interaction among the adsorbed species.

Clearly, any theory describing all possible lateral interactions on a large lattice would be of enormous complexity. The approximation scheme of Hijmans and de Boer provides a very systematic method for simplification of this problem. The actual lattice is replaced with sets of representative assemblies, or arrays, in which each constituent member consists of only a limited number of sites. The number of microvariables required in the physical description of such assemblies is then rather small, and it is possible to determine explicitly the thermodynamic properties of these assemblies. By increasing the complexity of the clusters in the arrays, the properties of the lattice can be approximated to any desired degree. Much of the subsequent discussion will therefore deal with the problem of decomposing any lattice into representative assemblies; once this has been accomplished, a specification of both the thermodynamic properties and the isotherms is relatively simple.

We now begin a consideration of the various steps involved in a general formulation of the theory. For purposes of illustration, we shall use the specific example of the hexagonal lattice depicted in Fig. 1.

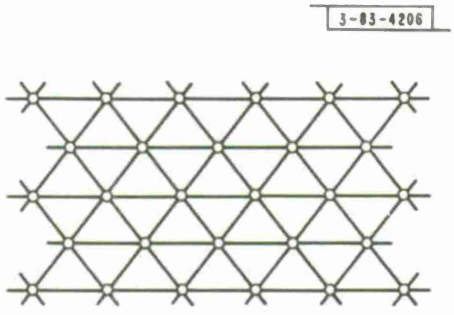

Fig. 1. Two-dimensional hexagonal lattice.

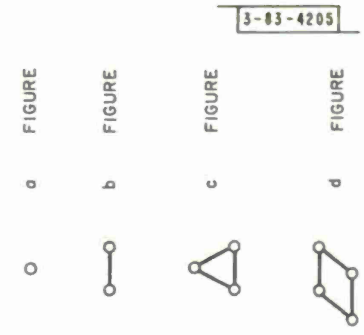

Fig. 2. Subfigures associated with hexagonal lattice.

TABLE I

VALUES FOR $x^{(m)}$ AND FOR $a^{(\ell)(m)}$ FOR HEXAGONAL LATTICE

	$a^{(\ell)(m)}$	m = 1	2	3	4
$x^{(a)} = 1$	$\ell = 1$	1	2	3	4
$x^{(b)} = 3$	2	0	1	3	5
$x^{(c)} = 2$	3	0	0	1	2
$x^{(d)} = 3$	4	0	0	0	1

y values

m	$x^{(m)}$	$y_a^{(m)}$	$y_b^{(m)}$	$y_c^{(m)}$	$y_d^{(m)}$
a	1	6	−5	1	1
b	3		3	−3	0
c	2			2	−4
d	3				3

II. DECOMPOSITION OF LATTICE INTO SUBFIGURES

The first step in the general Hijmans-de Boer procedure is to decompose the lattice into subfigures. These will be distinguished by the use of superscripts (a), (b), . . . (n), where (n) is reserved for the largest subfigure to be considered, which is termed the basic figure. The hexagonal lattice and some of the simpler subfigures designated by the running index (m) are shown in Figs. 1 and 2.

The number of subfigures of type (m) contained in any lattice is designated as $x^{(m)}L$, where L is the total number of lattice points. The procedure for obtaining numerical values for the $x^{(m)}$ is similar to that used in determining the number of atoms in a unit cell of a crystal. For example, in Fig. 1, $x^{(b)} = 3$ because every bond comprises two points, and every point represents the intersection of six lines. In finding $x^{(d)}$, it must be noted that every lattice point is common to twelve rhombi. A listing of several $x^{(m)}$ values is provided in Table I.

The subfigures specified by (a) and (b) are frequently termed points and bonds, respectively; those corresponding to x = c, d, etc., are designated by their geometric shape.

Every subfigure except the point (a) contains a certain number of simpler subfigures; the number of subfigures of type (ℓ) contained in the subfigure (m) will be designated by $a^{(\ell)(m)}$. For example, $a^{(a)(c)} = 3$, since each triangle contains 3 points. Table I contains a listing of several $a^{(\ell)(m)}$ values for the hexagonal lattice. Concerning $a^{(b)(d)}$ and $a^{(c)(d)}$, one must note that the rhombus is considered as consisting of two triangles, but of five rather than six bonds; that is, the base line common to the two triangles is counted only once. For purposes of this report we confine the theoretical treatment to the case where the rhombus is chosen as the basic figure.

III. OCCUPATION STATES OF VARIOUS SUBFIGURES

In the second step of the procedure we consider the various possible occupation states of the subfigures; i.e., we specify not only the number of occupied points in a given (m) figure, but also the manner in which these are distributed among the sites making up the (m) figure. Only nonequivalent configurations need be distinguished; these represent arrangements of the occupied sites that cannot be duplicated by carrying out symmetry operations on the subfigure as a whole. For example, the configurations shown in Fig. 3(a) are equivalent, since by the process of rotation of the triangles, both the occupied and the unoccupied sites can be brought into coincidence. On the other hand, the configurations shown in Fig. 3(b) are nonequivalent, since it is not possible to superpose the rhombi in such a way that all the occupied and unoccupied sites match. To

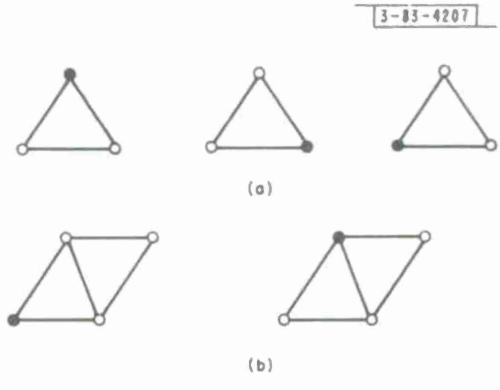

Fig. 3. Examples of equivalent and nonequivalent occupation states.

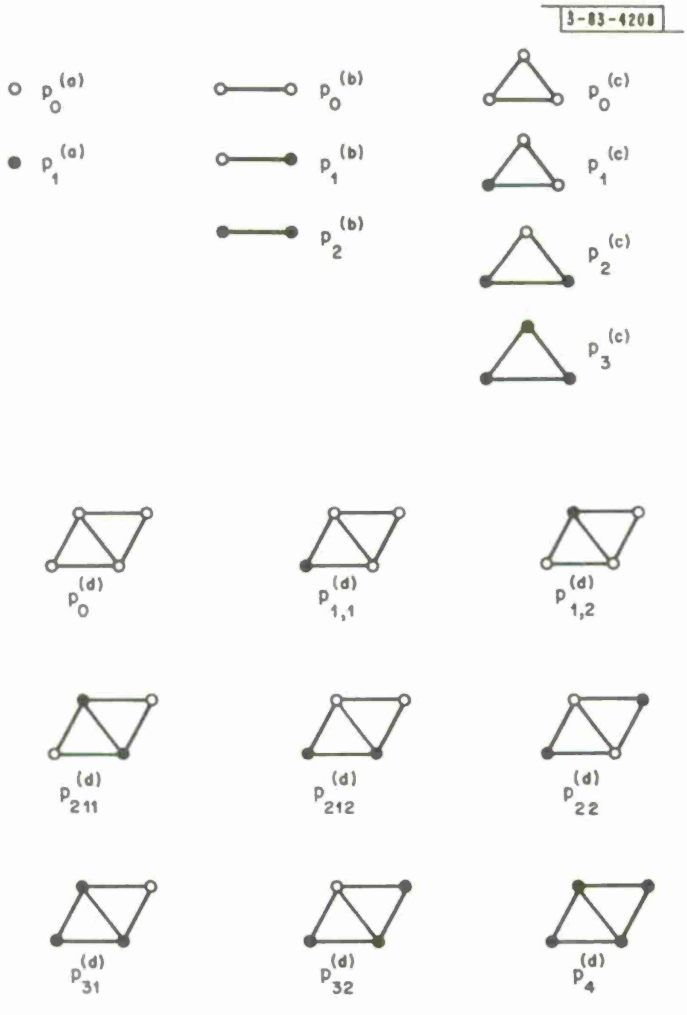

Fig. 4. Nonequivalent occupation states for subfigures of hexagonal, two-dimensional lattice, with designations for distribution numbers.

distinguish the various occupation states, we introduce the integer j, which denotes the number of sites occupied in a given subfigure. This is followed by the integer ξ, if needed, to distinguish between various possible arrangements of the j occupied sites among the possible positions in the subfigure. Finally, the integer r is introduced to distinguish between configurations that exhibit the same general relative pattern of the occupied sites but which involve nonequivalent sites. A listing of the various possible nonequivalent occupation states for subfigures of the hexagonal lattice is given in Fig. 4. Inspection of the rhombus shows that for j = 2 it is clearly necessary to distinguish the cases where the occupied points are adjacent (ξ = 1), or separated by the long diagonal (ξ = 2). When ξ = 1, one must specify whether the occupied sites form the short diagonal (r = 1) or one of the edges (r = 2). The above-mentioned indices are used as subscripts to the occupation probability, denoted by p.

With each occupation state, one associates a distribution number or occupation probability $p^{(m)}_{j\xi r}$ which indicates the fraction of all (m) figures in the (m)-figure assembly that are in the configuration jξr. A comma between subscripts [such as in $p^{(d)}_{1,2}$] indicates that the integer ξ is missing and that the two integers written out are associated with j and r, respectively. The absence of such a comma [as in $p^{(d)}_{32}$] shows that the integer r is missing and that the subscripts are to be identified with j and ξ.

Whenever a given occupation state can be specified in several equivalent configurations, the multiplicity factor $\lambda^{(m)}_{j\xi r}$ is introduced; for example, $\lambda^{(c)}_{2} = 3$, because the bond may lie along any one of the three sides of the triangle.

IV. DECOMPOSITION OF LATTICE IN FIGURE ASSEMBLIES

The third step requires the decomposition of the lattice into figure assemblies; this is one of the cardinal points in the Hijmans-de Boer method. For, if the lattice decomposition is properly achieved, then, to a good degree of approximation, the statistical properties of the simpler figures should reflect those of the lattice.

To illustrate the proper method of procedure, we regard the basic array as the (n) figures; from the calculations set forth in Sec. III we can compute the number of members $x^{(n)}$ in the (n)-figure assembly. Except in the trivial case (n) = (a), every basic figure contains further subfigures, designated by (m), (ℓ), . . . , (a). Thus, in setting up the (n)-figure assembly, we automatically include the $a^{(m)(n)}x^{(n)}L$ figures of type (m), the $a^{(\ell)(n)}x^{(n)}L$ figures of type (ℓ), . . . , and the $a^{(a)(n)}x^{(n)}L$ points contained in the $x^{(n)}L$ figures of type (n). Let these various quantities be listed at the very left in the equations below. Proceeding to the first relation, we notice that the actual number of (m) figures in the lattice is given by $x^{(m)}L$, whereas the number included in the (n)-figure assembly is $a^{(m)(n)}x^{(n)}L$. Any discrepancy between these two counts must be rectified by setting up an (m)-figure assembly of $y^{(m)}_{n}L$ members, where $y^{(m)}_{n}$ satisfies the relation (1). Note that $y^{(m)}_{n}$ may be positive, negative, or zero, according as $a^{(m)(n)}x^{(n)}L$ represents an undercount, overcount, or the proper count relative to the correct value $x^{(m)}L$. However, while only the $y^{(m)}_{n}L$ members are formally listed in the (m)-figure assembly, a different number, $a^{(m)(n)}x^{(n)}L$, are also implicitly present – these having been automatically included in the process of setting up the basic (n)-figure array. Thus, the totality of implicitly and explicitly occurring units in a given figure assembly is always positive.

As soon as the collection consisting of $y^{(m)}_{n}L$ units of type (m) was set up, a total of $a^{(\ell)(m)}y^{(m)}_{n}L$ units of type (ℓ), $a^{(k)(m)}y^{(m)}_{n}L$ units of type (k), . . . , and of $a^{(a)(m)}y^{(m)}_{n}L$ points

was automatically included with this set. Let these be listed as second terms in the equations; we then repeat the preceding argument with reference to Eq. (2): The correct count of (ℓ) figures in the lattice is $x^{(\ell)}L$. In general, we must now set up an (ℓ)-figure assembly by $y_n^{(\ell)}L$ members, such that the totality of (ℓ) figures – including those contained in the (n)- and (m)-figure assemblies – yields the correct quantity, that is, $x^{(\ell)}L$. Proceeding similarly, we can work our way down to the last equation involving the point figure. This type of argument leads to the set of relations:

$$a^{(m)(n)}x^{(n)} + y_n^{(m)} = x^{(m)} \tag{1}$$

$$a^{(\ell)(n)}x^{(n)} + a^{(\ell)(m)}y_n^{(m)} + y_n^{(\ell)} = x^{(\ell)} \tag{2}$$

$$a^{(k)(n)}x^{(n)} + a^{(k)(m)}y_n^{(m)} + a^{(k)(\ell)}y_n^{(\ell)} + y_n^{(k)} = x^{(k)} \tag{3}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$a^{(a)(n)}x^{(n)} + a^{(a)(m)}y_n^{(m)} + a^{(a)(\ell)}y_n^{(\ell)} + a^{(a)(k)}y_n^{(k)} + \ldots + y_n^{(a)} = x^{(a)} \tag{4}$$

Beginning with Eq. (1), since $a^{(m)(n)}x^{(n)}$ and $x^{(m)}$ are known, we can determine $y_n^{(m)}$, use it in Eq. (2) to find $y_n^{(\ell)}$, and proceed down the line to $y_n^{(a)}$.

By means of the above scheme we have thus succeeded in representing the lattice by figure assemblies consisting of: $x^{(n)}L$ members of type (n), $y_n^{(m)}L$ members of type (m), . . . , and $y_n^{(a)}L$ points, with a grand total of $\sum_{m=a}^{n} Ly_n^{(m)}$ members [we define $y_n^{(n)} \equiv x^{(n)}$].

In order to make certain that no type of subfigure has been missed nor that any extraneous type has been introduced, Hijmans and de Boer established the following procedure: Two basic (n) figures are overlapped until all possible first generation overlap figures are obtained. All possible pairs of these are overlapped until all possible second generation overlap subfigures are specified. The process continued until the overlap possibilities are completely exhausted; i.e., until the final generation of overlap figures contains only points. In conjunction with this process, one defines essential overlap figures as those which do not occur in subsequent generations. It can be proved[4] that the listing of essential overlap figures exhausts the set which is required for representation of the lattice as a series of figure assemblies.

V. STATISTICAL PROPERTIES OF FIGURE ASSEMBLIES

Having decomposed the lattice into representative figure assemblies, we now turn to a statistical treatment, regarding the constituent members in each assembly as completely independent of one another. One begins with a consideration of the number of ways in which all possible occupation states $j\xi r$, consistent with the (m) figure, can be distributed among the $y_n^{(m)}$ members of the (m)-figure assembly. The standard combinatorial expression for the number of possible complexions is given by

$$\Omega\,[y_n^{(m)};\ p_{j\xi r}^{(m)}] = \frac{[y_n^{(m)}L]!}{\prod_{j\xi r} [(p_{j\xi r}^{(m)}\, y_n^{(m)}L)!]^{\lambda_{j\xi r}^{(m)}}} \tag{5}$$

The quantity $p_{j\xi r}^{(m)} y_n^{(m)} L$ represents the number of (m) figures in the designated configuration. A product of this type is taken over the possible configurations, each factorial term being raised to the power of the corresponding multiplicity. Since L is large, one may employ Stirlings' approximation to obtain

$$\Omega\,[y_n^{(m)};\ p_{j\xi r}^{(m)}] = \left[\frac{y_n^{(m)} L}{e}\right]^{y_n^{(m)} L} \Bigg/ \prod_{j\xi r} \left[\frac{p_{j\xi r} y_n^{(m)} L}{e}\right]^{p_{j\xi r}^{(m)} \lambda_{j\xi r}^{(m)} y_n^{(m)} L} \quad . \tag{6}$$

The quotient $[y_n^{(m)} L/e]$ is independent of the configuration under study; therefore, this quantity may be written out as a factor, ahead of the product sign in the denominator of Eq. (6). This factor has the form

$$[y_n^{(m)} L/e]^{\left[\sum_{j\xi r} \lambda_{j\xi r}^{(m)} p_{j\xi r}^{(m)}\right] y_n^{(m)} L} \quad ;$$

in view of the normalization conditions (see Sec. VI), this factor reduces to the same form as the numerator of Eq. (6). Thus, we obtain

$$\Omega\,[y_n^{(m)}, p_{j\xi r}^{(m)}] = \left\{ \prod_{j\xi r} [p_{j\xi r}^{(m)}]^{\lambda_{j\xi r}^{(m)} p_{j\xi r}^{(m)} y_n^{(m)} L} \right\}^{-1} \quad . \tag{7}$$

The same line of reasoning may be pursued for the remaining types of figure assemblies. In each case one arrives at Eq. (7) only the index (m) being changed; the total number of complexions is therefore given by

$$W = \prod_{m=a}^{n} \Omega\,[y_n^{(m)}, p_{j\xi r}^{(m)}] \quad . \tag{8}$$

Thus far, a statistical description has been furnished for the independent members in the various figure assemblies. A postulate is now needed, showing how the properties of the lattice may be deduced from those of the figure assemblies. This postulate has been stated in a variety of ways.[4] Each formulation is equivalent to the assumption that the results deduced from Eqs. (7) and (8) are also applicable to the lattice proper. This obvious oversimplification enormously reduces the mathematical complexity of the problem under study.

As is well known, the combinatorial factor W is related to the entropy of the system under consideration: $S = k \ln W$. From Eqs. (7) and (8), we see that this leads to the relation

$$S_c = -kL \sum_{m=a}^{n} y_n^{(m)} \sum_{j\xi r} \lambda_{j\xi r}^{(m)} p_{j\xi r}^{(m)} \ln p_{j\xi r}^{(m)} \quad . \tag{9}$$

Note that this represents only the configurational contribution to the total entropy; the thermal contribution must be specified separately. We adjoin to this expression the energy contribution, exclusive of the thermal contribution, as given by

$$E_c = L \sum_{m=a}^{n} y_n^{(m)} \sum_{j\xi r} \lambda_{j\xi r}^{(m)} p_{j\xi r}^{(m)} \epsilon_{j\xi r}^{(m)} \quad . \tag{10}$$

In this equation, $\epsilon^{(m)}_{j\xi r}$ is the energy associated with one (m) figure in the configuration $j\xi r$. The energy due to all units of the (m)-figure assembly in this configuration is $\lambda^{(m)}_{j\xi r} p^{(m)}_{j\xi r} \epsilon^{(m)}_{j\xi r}$. This quantity is summed, first over all possible configurations consistent with the (m) figures, and then over all figure assemblies, to give the total energy.

VI. CONCEPT OF OCCUPIED SUBFIGURE

In principle, one could combine Eqs. (9) and (10) into an expression for the free energy and minimize this relation to characterize the equilibrium conditions. The principal difficulty in this procedure is that both S_c and E_c are functions of the various $p^{(m)}_{j\xi r}$; not all of these probabilities are linearly independent, however. Accordingly, it is necessary to decide on a set of independent variables with respect to which the minimization can be carried out. One systematic procedure for accomplishing this purpose is to introduce the concept of the occupied subfigure (s) belonging to the subfigure (m). Suppose k out of m points are occupied in the subfigure of type (m). Then the occupied subfigure refers to the geometric patterns of the k occupied sites abstracted from all the sites comprising the (m) figure. The nature of this concept will be clarified in conjunction with the discussion concerning Fig. 5, as given later in this section. Let us temporarily continue with the determination of mathematical properties.

The distribution number for the occupied subfigure will be represented by the symbol $q^{(m)}_{k\eta s}$. To relate the $q^{(m)}_{k\eta s}$ with the $p^{(m)}_{j\xi r}$, one introduces the factor $c^{(m)}_{k\eta s;j\xi r}$, which specifies in how many ways the occupied subfigure in the arrangement $k\eta s$ can be included among the j occupied sites of the (m)-figures in the configuration $j\xi r$. Methods for determining this particular coefficient will be given later. For the present, it is to be noted that the product $c^{(m)}_{k\eta s;j\xi r} \cdot \lambda^{(m)}_{j\xi r} p^{(m)}_{j\xi r} x^{(m)} L$ gives the number of occupied subfigures in the arrangement $k\eta s$ that arise from the members of the (m)-figure assembly in the occupation state $j\xi r$. Upon summing over this last set of indices, one finds the total number of occupied subfigures in the configuration $k\eta s$, obtained from the decomposition of the lattice. On the other hand, this quantity is also given by $\lambda^{(m)}_{k\eta s} q^{(m)}_{k\eta s} x^{(m)} L$, as follows from the definition of $q^{(m)}_{k\eta s}$. On equating these expressions one obtains

$$\lambda^{(m)}_{k\eta s} q_{k\eta} \equiv \lambda^{(m)}_{k\eta s} q^{(m)}_{k\eta s} = \sum_{j\xi r} c^{(m)}_{k\eta s;j\xi r} \lambda^{(m)}_{j\xi r} p^{(m)}_{j\xi r} \quad , \quad m = a, \ldots, n \quad \text{(all k)} \quad . \tag{11}$$

For the moment let us ignore the expression to the left of the identity sign.

The utility of Eq. (11) emerges upon examination of the conditions which must be satisfied by the $q^{(m)}_{k\eta s}$. The various $p^{(m)}_{j\xi r}$ relate to occupied states for members in the figure assemblies, whereas the $q^{(m)}_{k\eta s}$ apply to occupied subfigures abstracted from these. The $q^{(m)}_{k\eta s}$ therefore are independent of any unoccupied sites required to make up the m-figure. We now show that the $q^{(m)}_{k\eta s}$ apply equally well when the occupied subfigures are considered as part of the lattice.

The following conditions are then imposed on the q: The value of a given $q^{(m)}_{k\eta s}$ should not depend on the particular set of sites which is occupied, so long as the relative position of all occupied sites remains the same. As an example, refer to Fig. 5. Clearly, the occupied subfigure EB retains its identity in the lattice whether it be regarded as an edge of the rhombus EBCD or as a short diagonal of the rhombus ABDE. On the other hand, if these particular rhombi were considered as members of a figure assembly, they would be assigned different configurations (i.e., 211 and 212) and different distribution numbers. Consequently, it is

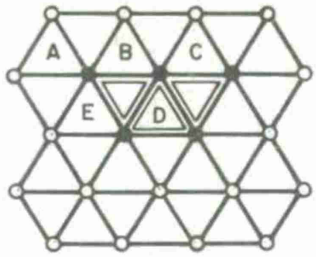

Fig. 5. Occupied subfigure in two-dimensional hexagonal lattice.

necessary to impose the condition $q^{(d)}_{211} = q^{(d)}_{212}$. This type of argument must be generally applicable and leads immediately to one condition to be met by the q-numbers:

$$q^{(m)}_{k\eta 1} = q^{(m)}_{k\eta 2} = \ldots = q^{(m)}_{k\eta} \quad . \tag{12}$$

Again, referring to Fig. 5, we observe that the line EB does not form part of any particular identifiable subfigure. For instance, line EB might be considered a fully occupied (b) figure, an edge of the triangle ABE or BDE, a short diagonal or edge of the rhombi previously mentioned, or it could be regarded as part of any higher subfigure. Once again, these various possibilities would be recognized as distinct in the figure assemblies and would be assigned separate occupation states and distribution numbers. However, since no such distinction is possible in the lattice, one must require that $q^{(b)}_{21} = q^{(c)}_{21} = q^{(d)}_{21} = \ldots$, or, more generally:

$$q^{(n)}_{k\eta} = q^{(m)}_{k\eta} = \ldots = q_{k\eta} \quad . \tag{13}$$

The smallest subfigure involved in Eq. (13) is that in which all sites are occupied; the largest is the basic (n) figure.

Equations of the form (12) and (13) are termed consistency requirements. On account of Eq. (11), they produce interrelations between the various $p^{(m)}_{j\xi r}$.

As a consequence of the consistency requirements, it is permissible to drop the superscript and the third subscript from the q symbol. Further, one must note the very important point that there exist only as many q numbers as there are occupied subfigures which can be distinguished in the lattice. The various $q_{k\eta}$ are therefore automatically independent.

At this point it is convenient to introduce the definition

$$c^{(m)}_{o;j\xi r} = 1 \text{ (all } j) \tag{14}$$

with which we obtain

$$q_o = \sum_{j\xi r} \lambda^{(m)}_{j\xi r} p^{(m)}_{j\xi r} = 1 \quad . \tag{15}$$

The relation on the left follows directly from use of the definition (14) in Eq. (11), whereas the equality on the right is a consequence of the definitions involving $\lambda^{(m)}_{j\xi r}$ and $p^{(m)}_{j\xi r}$, respectively. The statement $q_o = 1$ thus is a convenient shorthand relation for the normalization conditions characterizing the $p^{(m)}_{j\xi r}$. The quantity q_o cannot be considered on the same footing as $q_{k\eta}$ $(k > 0)$, since the state $k = 0$ represents a figure with no occupied sites. Clearly, no such occupied subfigure can be constructed, and so q_o is not a proper member of the set of distribution numbers q.

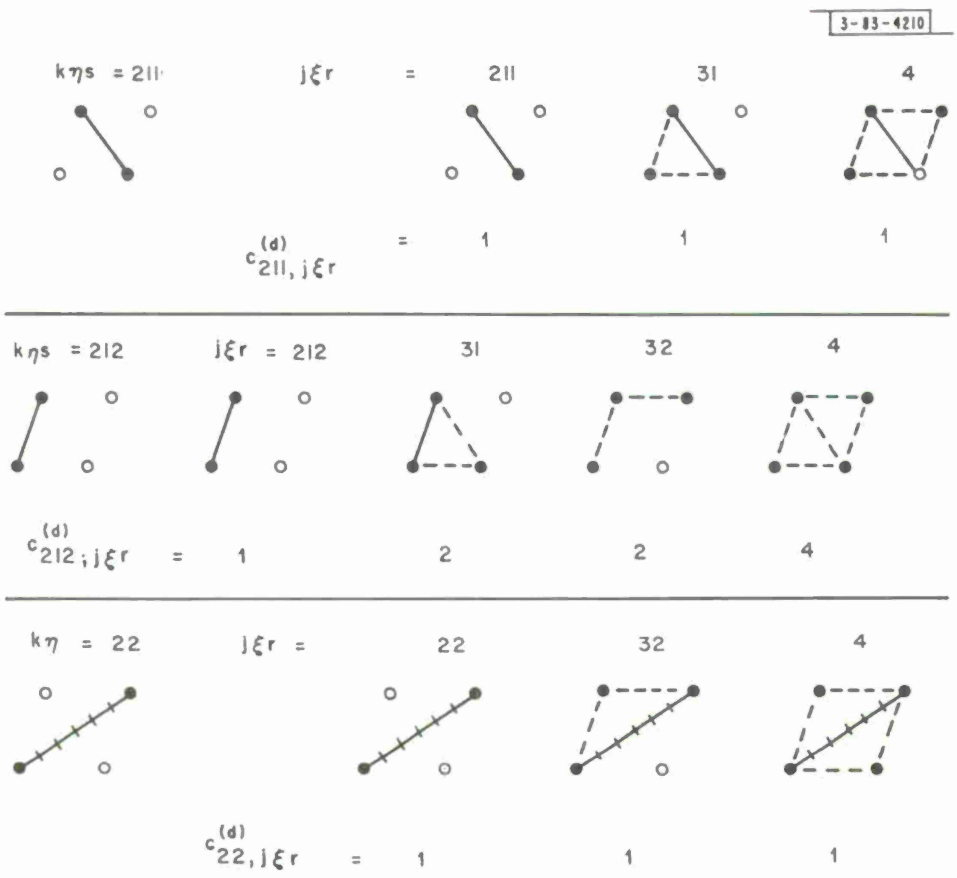

Fig. 6. Examples illustrating determination of elements in τ matrix.

We now take advantage of the previously stated linear independence of the various $q_{k\eta}$. For, if we succeed in inverting Eq. (11) as

$$\lambda^{(m)}_{j\xi r} p^{(m)}_{j\xi r} = \sum_{k\eta s} C^{(m)}_{j\xi r;k\eta s} \lambda^{(m)}_{k\eta s} q_{k\eta} \quad , \quad m = a, b, \ldots, n \quad \text{(all j)} \tag{16}$$

then it is possible to replace the variables $p^{(m)}_{j\xi r}$ by $q_{k\eta}$ and ultimately, to construct an expression for free energy of the system solely in terms of the linearly independent $q_{k\eta}$. The free energy can then be properly minimized.

Before Eq. (16) can be used, we need to determine the elements $C^{(m)}_{j\xi r;k\eta s}$. Fortunately, these quantities are very simply related to the elements appearing in Eq. (11); as will be shown, the two sets differ at most in sign. Since $c_{k\eta s;j\xi r}$ can be readily obtained by inspection of the figure assemblies, the determination of the coefficients in Eq. (16) represents no problem. We will designate the matrices with elements $C^{(m)}_{j\xi r;k\eta s}$ and $c^{(m)}_{k\eta s;j\xi r}$ by T and τ, respectively.

VII. DETERMINATION OF $c^{(m)}_{k\eta s;j\xi r}$; DIGRESSION OF PROOF THAT MATRIX ELEMENTS OF T AND τ DIFFER AT MOST IN SIGN

At this point we show how the matrices τ and T may be constructed. The general method of finding the elements $c^{(m)}_{k\eta s;j\xi r}$ follows the scheme depicted in Fig. 6 in which (m) = (d), and k = 2, j = 2, 3, or 4. For example, $c^{(d)}_{212;31} = 2$ because the line segment [here the occupied subfigure (b)] which forms an edge of the rhombus in the occupation state 212 can be laid along either edge of the (d) figure in the occupied state 31. It cannot be superposed with the short diagonal of the (d) figure in the configuration 31; for, such an operation is possible only when the occupied subfigure (b) is in the configuration 211.

Values of the matrix elements for several subfigures of τ together with the proper multiplicities are entered in Table II. Attention is directed to the following points:

(a) All elements of τ are nonnegative.

(b) All elements below the diagonal vanish identically, since it is impossible to superpose an occupied subfigure on a subfigure with a smaller number of sites.

(c) All diagonal elements are unity, since a given occupied subfigure can be superposed on itself in only one way.

(d) The top row elements are unity because of the definition (14).

(e) The elements in the last column coincide with the multiplicities; i.e., when an occupied subfigure (s) is matched with an (m) figure, all of whose sites are also occupied, then all possible ways of including the k points of the (s) figure in the j points of the (m) figure must be included. This latter type of process is exactly analogous to that used in determining the multiplicities.

We turn now to the proof of the fact that the matrix elements of τ and T differ at most in sign. This proof rests on the following important relation which holds only for fixed k:

$$\sum_{\eta s} c^{(m)}_{k\eta s;j\xi r} = j!/k!\,(j-k)! \qquad \text{(k fixed)} \tag{17}$$

To verify Eq. (17), we observe that a variation in the indices η and s corresponds to a change in the relative position of the k points comprising the (s) figure. A nonzero contribution to the

TABLE II

T OR τ MATRICES FOR TRIANGULAR LATTICE
(The minus sign obtains for elements of T matrix)

a	$\lambda_i^{(a)}$	1	1
$\lambda_k^{(a)}$	k \ i	0	1
1	0	0	±1
1	1	0	1

b	$\lambda_i^{(b)}$	1	2	1
$\lambda_k^{(b)}$	k \ i	0	1	2
1	0	0	±1	1
2	1	0	1	±2
1	2	0	0	1

c	$\lambda_i^{(c)}$	1	3	3	1
$\lambda_k^{(c)}$	k \ i	0	1	2	3
1	0	1	±1	1	±1
3	1	0	1	±2	3
3	2	0	0	1	±3
1	3	0	0	0	1

d	$\lambda_{i\xi r}^{(d)}$	1	2	2	1	4	1	2	2	1
$\lambda_{k\eta s}^{(d)}$	k \ i	0	1,1	1,2	211	212	22	31	32	4
1	0	1	±1	±1	1	1	1	±1	±1	1
2	1,1	0	1	0	±2	±1	0	2	1	±2
2	1,2	0	0	1	0	±1	±2	1	2	±2
1	211	0	0	0	1	0	0	±1	0	1
4	212	0	0	0	0	1	0	±2	±2	4
1	22	0	0	0	0	0	1	0	±1	1
2	31	0	0	0	0	0	0	1	0	±2
2	32	0	0	0	0	0	0	0	1	±2
1	4	0	0	0	0	0	0	0	0	1

sum over η and s is obtained only if, on a particular arrangement, all units of the (s) figure coincide with occupied sites of the (m) figure. Otherwise, the corresponding $c^{(m)}_{k\eta s;j\xi r}$ vanishes, as follows immediately from the definition of this quantity. Thus, in carrying out the summation on the left of (17), we exhaust all possible distributions of k particles among j locations; the number of ways in which this can be done is shown by the combinatorial expression on the right.

It is now asserted that

$$C^{(m)}_{k\eta s;j\xi r} = (-1)^{(j-k)}\, c^{(m)}_{k\eta s;j\xi r} \quad . \tag{18}$$

If Eq. (18) is correct, then all elements of the product matrix would have to satisfy the requirement

$$\sum_{k\eta s} (-1)^{(j-k)}\, c^{(m)}_{\ell\zeta t,k\eta s} c^{(m)}_{k\eta s,j\xi r} = \delta_{j\ell}\delta_{\xi\zeta}\delta_{rt} \tag{19}$$

where the symbols on the right are the conventional Kronecker deltas. The quantity on the left is the element ($\ell\zeta t$, $j\xi r$) of the matrix $T\tau$.

Thus, if we can establish Eq. (19), the assertion (18) is proved. We show that Eq. (19) is correct by separating the summations over η and s from that over k. Then the left-hand side of the above equation becomes

$$\sum_{k} (-1)^{(j-k)} \sum_{\eta s} c^{(m)}_{\ell\zeta t;k\eta s} c^{(m)}_{k\eta s;j\xi r} = \sum_{k} (-1)^{(j-k)} \frac{(j-\ell)!}{(j-k)!\ (k-\ell)!} \quad . \tag{20}$$

The expression on the right follows from an argument similar to that given in conjunction with Eq. (17). Keeping k fixed, a variation in the indices η and s corresponds to a change in the relative arrangement of the k points of the occupied subfigure (s). If there is to be any contribution to the sum on the left-hand side, neither the first nor the second factor can be allowed to vanish. This means that the configuration $\ell\zeta t$ must be such that all points associated with it are superposed on occupied points of the (m) figure in the occupation state $k\eta s$; similarly, the latter, considered now as an occupied subfigure, must have all of its sites coincide with the (m) figure in the configuration $j\xi r$. Briefly, the $k\eta s$ configuration must be intermediate between $j\xi r$ and $\ell\zeta t$. This means that we are not allowed to change the k points at random; ℓ among these must remain in a fixed position dictated by the given configuration $\ell\zeta t$, the remaining $(k-\ell)$ points can assume only those positions coincident with the $(j-\ell)$ remaining occupied sites of the (m) figure in the configuration $j\xi r$. In effect, the summation represents a rearrangement of $(k-\ell)$ particles among $(j-\ell)$ possible locations; the number of ways in which this can be accomplished is shown on the right of Eq. (20).

If we next sum over k, we observe that $\sum_{k} (-1)^{(j-k)}\, (j-\ell)!/(j-k)!(k-\ell)!$ vanishes identically except when $j = \ell\ (=k)$; for a proof, the reader is referred to standard texts.[8] Thus, the sum (20) generally vanishes; however, if $j = k = \ell$, then it reduces to the single term $0!/0!\ 0! = 1$. So far, we have established that the left-hand side of Eq. (19) is equal to $\delta_{j\ell}$; the remaining Kronecker deltas are obtained by the argument that when $j = k = \ell$, all figures contain the same number of sites and are superposable only if the geometric arrangement of the occupied sites is the same. Assertion (18) is thus proved.

One further property of the matrix is needed

$$\sum_{k\eta s} C_{k\eta s;j\xi r} \begin{cases} = 0 & \text{for} \quad \text{all } j > 0 \\ = 1 & \text{for} \quad j = k = 0 \end{cases} \tag{21}$$

To prove this, substitute Eq. (18) on the left and take account of Eq. (17). The resulting sum is

$$\sum_{k} (-1)^{(j-k)} \frac{j!}{k!\,(j-k)!} = \sum_{k} (-1)^{(j-k)} \frac{(j-0)!}{(k-0)!\,(j-k)!} \quad . \tag{22}$$

From the mathematical properties of this type of summation[8] it follows that Eq. (22) vanishes except when j = 0 (=k). This establishes Eq. (21).

VIII. EQUATIONS CHARACTERIZING EQUILIBRIUM STATES OF SYSTEM

We have now set the stage for deriving equations that characterize equilibrium states of the system under a prescribed set of conditions. We begin with the basic thermodynamic relation $F_c = E_c - TS_c$, into which we substitute from Eqs. (9) and (10). This yields

$$F_c = L \sum_{m=a}^{n} y_n^{(m)} \sum_{j\xi r} \lambda_{j\xi r}^{(m)} p_{j\xi r}^{(m)} \left[\epsilon_{j\xi r}^{(m)} + kT\ell n\, p_{j\xi r}^{(m)}\right] \quad . \tag{23}$$

In minimizing F_c to find the equilibrium properties of the system, we consider the $q_{k\eta}$ to be the independent variables. Accordingly, it follows that

$$\delta F(q_{k\eta}) = \sum_{k\eta} \frac{\partial F}{\partial q_{k\eta}} \delta q_{k\eta} = 0 \qquad (k > 0) \quad . \tag{24}$$

In view of the fact that Eq. (24) must hold, whatever the variations in the $q_{k\eta}$, the coefficient of every $q_{k\eta}$ must itself vanish identically. This leads to the set of conditions

$$0 = \frac{\partial}{\partial q_{k\eta}} \left\{ L \sum_{m=a}^{n} y_n^{(m)} \sum_{j\xi r} \lambda_{j\xi r}^{(m)} p_{j\xi r}^{(m)} \left[\epsilon_{j\xi r}^{(m)} + kT\ell n\, p_{j\xi r}^{(m)}\right] \right\}$$

$$\text{(all } k\eta \text{ for which } k > 0) \quad . \tag{25}$$

Upon carrying out the indicated differentiation, one finds

$$0 = L \sum_{m=a}^{n} y_n^{(m)} \sum_{j\xi r} \lambda_{j\xi r}^{(m)} \left[\epsilon_{j\xi r}^{(m)} + kT\ell n\, p_{j\xi r}^{(m)} + kT\right] \frac{\partial p_{j\xi r}^{(m)}}{\partial q_{k\eta}} \quad . \tag{26}$$

The differentials may then be computed from Eq. (16) as shown below:

$$\frac{\partial p_{j\xi r}^{(m)}}{\partial q_{k\eta}} = \sum_{s} C_{j\xi r;k\eta s}^{(m)} \frac{\lambda_{k\eta s}^{(m)}}{\lambda_{j\xi r}^{(m)}} \tag{27}$$

and when this last relation is used in Eq. (26) one obtains

$$0 = L \sum_{m=a}^{n} y_n^{(m)} \sum_{j\xi r} \left[\epsilon_{j\xi r}^{(m)} + kT\ell n\, p_{j\xi r}^{(m)} + kT\right] \sum_{s} C_{j\xi r;k\eta s}^{(m)} \lambda_{k\eta s}^{(m)} \quad . \tag{28}$$

We now invert the order of the summations. In so doing, the third term in the summation of Eq. (28) reads

$$kT \sum_{s} \lambda^{(m)}_{k\eta s} \sum_{j\xi r} C^{(m)}_{j\xi r;k\eta s} \quad .$$

On applying Eq. (21), after interchange of the set of indices, this contribution is found to vanish (q_0 not being a proper variable for inclusion among the set of distribution numbers). Eq. (28) can thus be put into the final form

$$\sum_{m=a}^{n} y_n^{(m)} \sum_{j\xi r} \left[\sum_{s} C^{(m)}_{j\xi r;k\eta s} \lambda^{(m)}_{k\eta s} \right] [\epsilon^{(m)}_{j\xi r} + kT \ell n \, p^{(m)}_{j\xi r}] = 0 \qquad (\text{all } k > 0) \qquad (29)$$

The set of equations (29) is known as equilibrium conditions; observe that these are again specified in terms of $p^{(m)}_{j\xi r}$. The normalization and consistency requirements mentioned earlier furnish further interrelations between the $p^{(m)}_{j\xi r}$. On the basis of this total set of equations it is possible to solve for the distribution numbers $p^{(m)}_{j\xi r}$ as a function of the parameters T and $\epsilon^{(m)}_{j\xi r}$.

IX. CONCLUDING REMARKS

The above section concludes the presentation of the main features of the Hijmans-de Boer approximation to order-disorder theory. The applications of this methodology to the treatment of gas adsorption have been fully described in several articles in the literature.

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13. ABSTRACT

In this report the Hijmans-de Boer approximation scheme to order-disorder theory is reviewed, with special reference to its ultimate application in the area of gas adsorption phenomena. The purpose of the exposition is to provide a more detailed description of the derivation and to assist the reader, wherever possible, in visualizing the fundamental scheme by a pictorial approach.

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